Chapter 5
Liquefied Dimethyl Ether: An Energy-Saving, Green Extraction Solvent

Peng Li and Hisao Makino

Abstract Extraction is an essential procedure in the fields of food, pharmacy, and renewable bio-fuels, and it affords the recovery of desired components and the removal of undesired components from the natural feedstock. Conventional extraction techniques involving organic solvents and supercritical fluids have been extensively studied and used. Generally, these techniques are either economically or environmentally unfavourable because of the use of toxic solvents and considerable heating and pressurizing. Recently, a new extraction technique involving the use of liquefied dimethyl ether (DME) as a green solvent has attracted tremendous attention. This technique is economically efficient and environmentally friendly by virtue of the unique physical and chemical properties of DME. Additionally, the DME method can extract/remove the desired/undesired components as well as dewater (dry) the wet materials simultaneously. These advantages render the DME method practicable in several industrial fields. This chapter attempts to outline the potential of liquefied DME as an extraction solvent by elucidating the operating principles, procedures, and some recent studies and results.

Keywords Extraction • Dimethyl ether • Dewatering

5.1 Introduction

Extraction techniques are widely employed for the isolation of various compositions from natural resources in industries pertaining to food and pharmacy, and is being considered employing in the field of renewable bio-fuels production from natural biomasses In some cases, the extraction technique is an essential step in

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eliminating the undesired components from the feedstock. Basically, extraction can be categorised based on the use of traditional solvents and critical fluids. The traditional solvent extraction is the most common because chemical solvents have high selectivity and solubility for the target compositions. In the traditional solvent extraction, the solvent used is in the liquid form at room temperature and ambient pressure. A wide range of organic solvents such as chloroform, methanol, hexane, and petroleum ether have been applied [1, 10]; the selection of solvent is usually dependent upon the type of target feedstock and target chemicals contained in the feedstock. The major factors that influence the efficiency and selectivity of solvent extraction are the physicochemical properties of the selected solvent such as polarity, and the operating conditions such as temperature. In addition, the economic and environmental concerns must be considered. The principle of the traditional chemical solvent extraction is as follows: an organic solvent is in contact with the extractable materials while the target compositions are continuously extracted into the organic phase because of the permeability effect of the solvent on the materials. The selection of the organic solvents is of tremendous relevance because it must possess biocompatibility, maximum solubility for target compositions, and extraction ability. The disadvantage of traditional solvent extraction is that most of the organic solvents cause health hazards and/or environmental pollution. Besides, pretreatment processes such as drying and cell disruption are normally required for the extraction of available components from natural resources, increasing the overall cost burden.

Supercritical fluid technology (SFT) is more efficient compared to traditional solvent extraction, and shows high selectivity. The basic principle of SFT involves the establishment of a certain phase (supercritical) which is beyond the critical point of the fluid, wherein the meniscus separating the liquid and vapour phases disappears, leaving behind a single homogeneous phase [27]. SFT is a suitable substitute for organic solvents for a range of industrial and laboratory processes. Carbon dioxide (CO_2) and water are the most commonly used supercritical fluids, which could be potentially used for the extraction of natural products. For example, supercritical CO_2 has several advantages over traditional solvents, especially for extracting less polar chemicals [11, 19]. The disadvantages of SFT are associated with the high costs of operation and safety related issues; for instance, in the case of supercritical CO_2, the operating temperature and pressure are above 304.25 K and 7.39 MPa, respectively. In order to reduce the costs, recent studies involving near- or sub- critical solvents such as dimethyl ether have been reported [2].

Central Research Institute of Electric Power Industry (CRIEPI) recently developed a new extraction technology that differs from both the traditional organic solvent extraction and SFT. This technique uses liquefied dimethyl ether (DME) as the solvent to extract the target compositions, and remove the water from the wet materials simultaneously. The advantages of this method are that it is highly cost-efficient and environmentally friendly. In fact, the use of DME as an extraction solvent has been approved by the European Union [6]. Thus far, this technique has been studied at both laboratory and bench scales for use in the (1) dewatering and extraction of organic components from vegetal biomasses [22];

(2) extraction of bioactive components from green tea leaves [18]; (3) extraction of lipids and hydrocarbons from high-moisture microalgae [14, 16, 17]; (4) removal of polychlorinated biphenyls (PCBs) from polluted soil and other materials [26]. A pilot-scale study on the use of DME for extraction purposes is also being carried out in CRIEPI.

This chapter presents a complete picture of the current knowledge and recent studies on the use of liquefied DME for extraction. It provides the necessary theoretical background and relevant details of the method including the technique, mechanism, and some recent results pertaining to the extraction of natural products.

5.2 Basic Principles

5.2.1 Properties of DME

The chemical structure of DME is shown in Fig. 5.1. DME is the simplest ether with the formula, CH_3OCH_3, which is in a gaseous state at room temperature and pressure. The standard boiling point of DME is −24.8 °C and its saturated vapour pressure has been previously mentioned and explained in detail [28]; for example, the pressure is 0.51–0.59 MPa over the normal temperature range of (20–25 °C). Like other organic solvents, DME has high affinity for organic compositions, but the difference is that it is also partially miscible in water. The phase equilibrium relationship for the liquefied DME/water system is known [9]. At room temperature, water is soluble in DME over the range of 7–8 wt%. For example, the weight of DME required for the extraction of water is 1/(0.07–0.08) times the weight of water. DME is almost non-toxic; the European Food Safety Authority has determined that there are no health concerns with regard to the use of DME as an extraction solvent in food processing [6].

5.2.2 Theoretical Principles of DME Extraction

A schematic depicting the steps involved in DME extraction is shown as Fig. 5.2. In the first step, the target components and/or water in the natural materials are extracted using liquefied DME; and as a result, a mixture of DME, water and organic components is formed. Secondly, the concentration of water and organic components in liquefied DME increases and reaches saturation, while the materials are dried. Thirdly, the DME in the mixture is vapourised, and then the organic components and water are separated. In the final step, the DME gas is again liquefied for the next circulation.

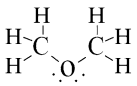

Fig. 5.1 Structure of DME molecule

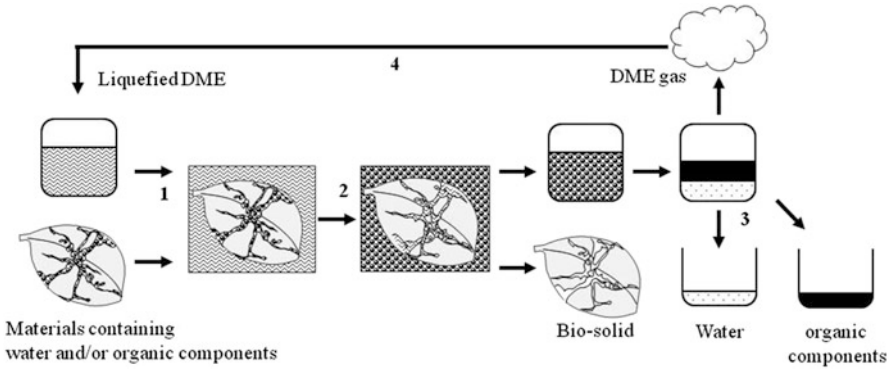

Fig. 5.2 Flow chart of process of DME extraction for wet natural feedstock

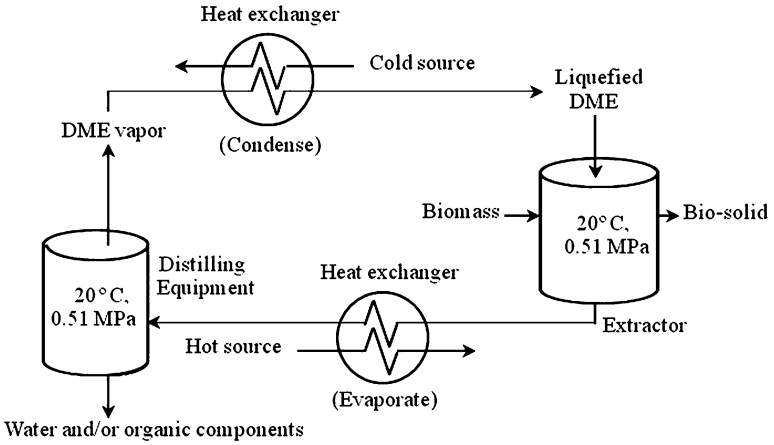

Fig. 5.3 Schematic illustration of the DME extraction system

The principle of energy saving in the aforementioned process is shown in Fig. 5.3, which represents a DME extraction system [22]. In this system, at ambient temperature, DME is mixed with organic components and water in an extractor, using which water and organic components are separated. By employing techniques such as filtration and sedimentation, the water-organic-DME mixture can be separated from the materials and ejected from the extractor. If the concentration of the organic components in the mixture is insufficient for further use, the mixture is recycled as the extractant. Next, the DME in the mixture is evaporated in a heat exchanger by a low-level waste heat. As a consequence, supersaturated water appears beneath the liquefied DME phase because the organic component dissolves more readily into the liquefied DME. The organic-DME mixture is then separated from the water layer, and most of the DME at this stage exists as a gas. The DME

vapour is condensed in the heat exchanger using cold heat sources. The reutilization of DME, including its evaporation and liquefaction, permits the efficient use of low-level heat source. For large-scale applications, a heating source of unharnessed waste heat at about 40 °C is desirable for DME evaporation. DME gas is then liquefied again at a slightly lower temperature for recirculation. At this stage, a cooling source of about 10 °C such as geo-heat, which is present within the first 50 m of the earth's surface, is desirable [4].

5.3 Experimental

5.3.1 Laboratory-Scale DME Extraction Apparatus

Kanda et al., designed the laboratory-scale apparatus to evaluate the extraction efficiency of the proposed method [13]. The apparatus mainly consisted of three parts generally; however, in order to test the different materials based on their respective properties, the apparatus was slightly modified. As shown in Fig. 5.4, a vessel for storing the liquefied DME (TVS-1-100, Taiatsu Techno Corp., Saitama, Japan), a vessel as extraction column (HPG-10-5 Taiatsu Techno Corp.) and a storage vessel to hold the mixture of DME, water and/or extracted organic components (HPG-96-3, Taiatsu Techno Corp.) were connected in series. The test materials were loaded into the extraction column. Nitrogen (0.6 MPa) was used to push the liquefied DME through the extraction system.

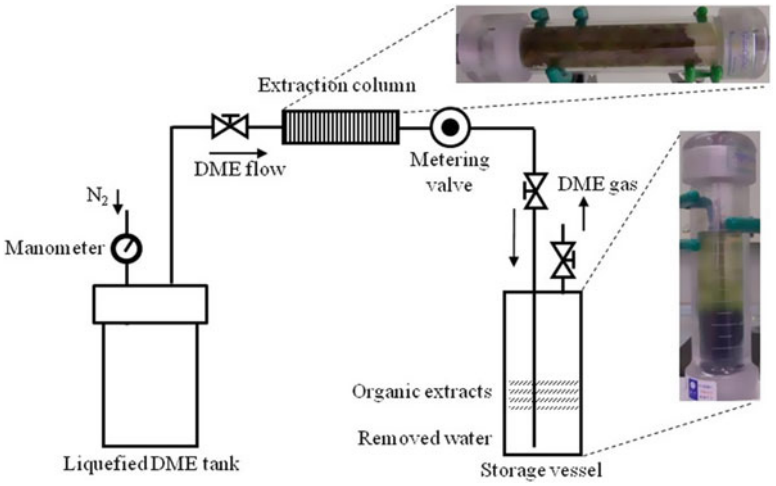

Fig. 5.4 Schematic diagram of the lab-scale DME extraction apparatus (the sample in the extraction column is green tea leaves)

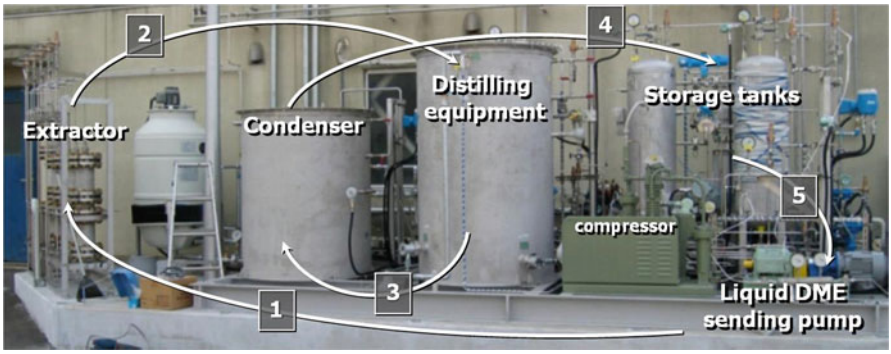

Fig. 5.5 The prototype of the DME extraction process

5.3.2 Bench-Scale DME Extraction Equipment

The world's first prototype of the DME extraction process was reported by Kanda and Makino as shown in Fig. 5.5 [12]. Briefly, the equipment consisted of a liquefied DME pump, extraction column (volume 0.01 m^3, inner diameter 0.15 m, length 0.55 m), evaporator, flash distillation tower (volume: 0.1 m^3), and condenser, connected in series to form a closed loop. In this extraction system, the operation pressure was 0.51 MPa, and temperature in the extractor and distillation tower was around 20 °C. Liquefied DME was mixed with wet test materials in the extractor, and water and organic compounds were extracted. The mixture of water, organic compounds and DME was separated from the test materials and ejected from the extractor. Next, DME in the mixture was evaporated in the heat exchanger at 30 °C, and the water and organic components were separated from DME in the distillation tower. The DME vapour was then condensed in the heat exchanger at 15 °C.

5.4 Results and Discussion

5.4.1 Extraction and Dewatering of Vegetal Biomass

Li et al., reported the extraction of three representative common vegetal biomasses including spent coffee grounds, green tea waste, and orange peels for validating the performance of DME extraction method. These materials are the main sources of industrial food waste generated on a huge scale worldwide, warranting their effective utilisation. For example, the world annually produces around 6 million tons of spent coffee grounds from the beverage factories [24]. According to a credible report, the spent coffee grounds contain around 10–15 % of oily substances, depending on the coffee species, which can be easily converted into biodiesel [20].

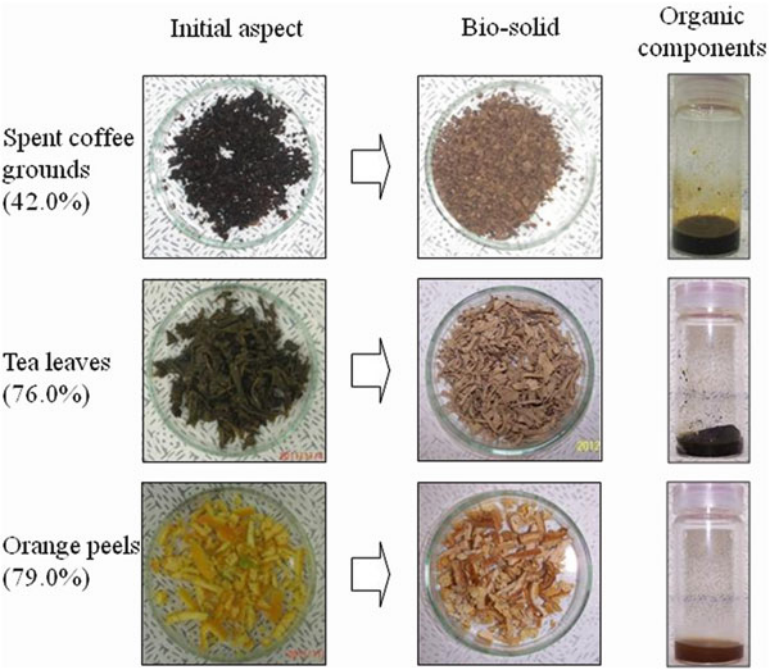

Fig. 5.6 Pictures of original samples, dewatered bio-solids and extracted organic components. The value in parentheses is the initial water content of biomass

Green tea is consumed worldwide as one of the most popular, traditional beverages, particularly in Asian countries such as China, India, and Japan. The annual global production of tea was about 4.51 million tons in 2010 [7].

As shown in Fig. 5.6, the surfaces of these vegetal biomasses became relatively brighter after DME extraction owing to a substantial decrease in the water and pigment contents of these samples. Figure 5.7 shows the changes in the water content of the test samples and amounts of the organic extracts in the storage vessel. As the amount of liquefied DME passing through the extraction system increased, the water content in samples decreased while the amount of organic extracts in the storage vessel significantly increased. When the amounts of consumed DME were 218.1, 196.9, and 200.5 g, the corresponding water contents in the samples were 5.0 %, 10.0 %, and 11.9 %, respectively. On the other hand, to obtain the maximum amounts of organic extracts from the spent coffee grounds and green tea waste, approximately 276.4 and 277.1 g of DME were consumed. The difference in the DME consumption for dewatering and extraction of organic components for spent coffee grounds and green tea waste may be due to the difference in the biologic properties of these biomasses. The results also implied that the dewatering velocity of the liquefied DME exceeded its extraction velocity for organic components, at least for spent coffee grounds and green tea waste.

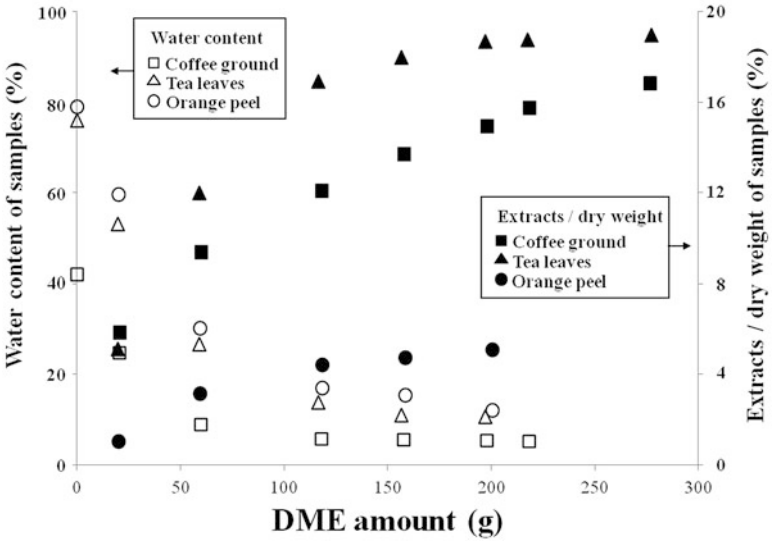

Fig. 5.7 Changes of water content in the samples and yield of organic extracts

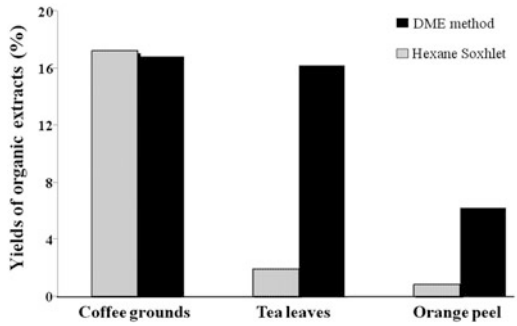

Fig. 5.8 Organic extracts yield using the DME (*black*) and hexane Soxhlet (*gray*) methods

The extraction yields of the organic components obtained using the DME extraction method were compared to those obtained from the widely-used conventional Soxhlet method involving hexane. As shown in Fig. 5.8, with the Soxhlet method, the extraction yields of the spent coffee grounds, green tea waste, and orange peels were 17.2 ± 0.2 %, 1.9 ± 0.1 % and 0.9 ± 0.05 %, respectively; however, the extraction yields using the DME method were 16.8 ± 1.0 %, 16.2 ± 1.5 %, and 6.2 ± 0.5 %, respectively. The difference in the extraction yields between the two methods was because of the difference in the chemical compositions of the tested biomasses and the chemical properties between DME and hexane.

Table 5.1 Sample details of tested algae varieties

	Genus	Cell form	Water content (%)	Location
N-595	*Oscillatoria agardhii*	Filar	85	Northern Ireland
N1263	*Oscillatoria agardhii*	Filar	85	Germany
ONC	*Microcystis aeruginosa*	Granular	93.4	Okinawa island (Japan)
GSK	*Microcystis aeruginosa*	Granular	91.1	Okinawa island (Japan)
GK12	*Monoraphidium chlorophyta*	Granular	78.2	–
Kanogawa	*Cymbela*	Acicular	93	Lake Kanogawa Ozu (Japan)
Hirosawa[a]	*Microcystis*	Granular	91	Hirosawa mere Kyoto (Japan)

[a]Microalgae sample was mixed-species

5.4.2 *Extraction of Bio-oils from Microalgae*

Fossil fuel depletion and global warming have impelled researchers to work on bio-fuel production from biomasses such as crops, animal fat, and microalgae [25]. Among these, microalgae have attracted significant attention as the newest generation of biofuel resource [8]. Compared to terrestrial plants, microalgae have high oil content and growth rate; mass algal cultivation can be performed on unexploited lands using systems supplying nutrients, thus avoiding competition with limited arable lands [21].

In the conventional process, the recovery of bio-oils from microalgae generally requires multiple solid-liquid separation steps. These processes involve drying, cell wall disruption, and solvent extraction [23]. The extraction of bio-oils is usually performed with toxic organic solvents such as hexane, chloroform, and methanol, which means these processes are highly energy-intensive and damaging to the environment [23]. For example, on the laboratory scale, bio-oil extraction with hexane is normally carried out using the Soxhlet method at 70 °C for 18 h [5]. Such long duration of extraction and heating is a key drawback. The most rapid and effective conventional extraction method for bio-oils is the Bligh-Dyer's method [1], which involves drying, cell disruption, and solvent (chloroform-methanol) extraction. This standard method has been indispensable, not only for bio-oil extraction from microalgae but also for the quantification of crude oil derived from biological materials [10].

Kanda et al., investigated the extraction of bio-oils using liquefied DME on several natural blue-green microalgae, and the results were compared to those obtained using the Bligh-Dyer's method [16]. The sample details of the tested algae are listed in Table 5.1. The extraction volumes achieved using liquefied DME and the Bligh-Dyer's method are shown in Fig. 5.9. White columns represent the bio-oil extraction yield using liquefied DME on the dry weight of the microalgae while the black columns represent the results of the Bligh-Dyer's method. Both NIES-595 and NIES-1263 belong to *Oscillatoria agardhii*, but their extraction yields were

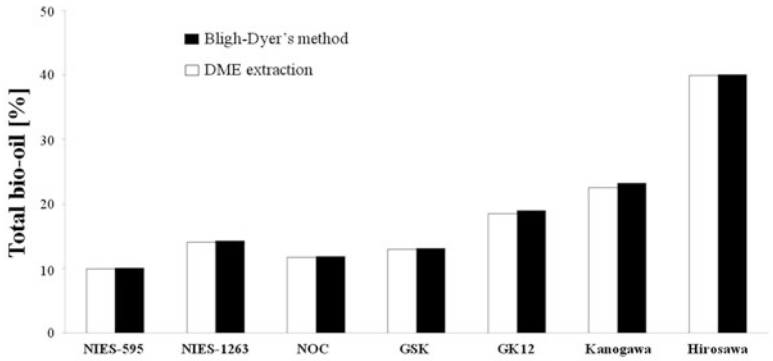

Fig. 5.9 Bio-oil extraction ratio using the DME and BD methods for several species of natural microalgae

9.9 ± 1 % and 14.0 ± 1 %, respectively. Conversely, the extraction rates of ONC 11.0 ± 2 % and GSK 12.0 ± 1.5 % were similar. The extraction yield of GK12 was 18.5 ± 2 % while that of the mixed-species of microalgae collected at Lake Kanogawa was 22.5 ± 1 %. The extraction yield of Hirosawa Mere showed the highest extraction rate at 40.1 ± 2 %. The extraction yield of all the species was more than 97.0 % as determined by the Bligh-Dyer's method. This implied that the extraction yields obtained using the DME extraction method were comparable to those obtained using the Bligh-Dyer's method.

In another recent study Kanda et al., proposed the use of this method to directly extract hydrocarbons from the wet *botryococcus braunii*, which is a fine energy source containing a considerable amount of hydrocarbons [17]. Our results indicated that the extraction yields of hydrocarbons using DME were approximately identical to those obtained using the Soxhlet extraction method involving hexane.

5.4.3 Other Recent Studies Involving DME

The use of DME not only affords the extraction of available components from natural feedstock but also the removal of water and undesired components. Oshita et al., successfully investigated the removal of PCBs and water from the river sediments [26]. The maximum extraction efficiencies of liquefied DME for PCBs and water were 99 % and 97 %, respectively. Only about 2 % of PCBs remained in the sediment after DME treatment. Kanda et al., proposed this method to remove the odorous components and water from the slurry of biosolids [15]. In their study, the moisture content of the test sludge cake was reduced from 78.9 to 8.0 %. The amounts of the odorous components in the dewatered sludge including hydrogen sulphide, methyl mercaptan, methyl sulphide, and acetaldehyde were reduced significantly.

Table 5.2 Balancing contents of caffeine and catechins

Amount (μg)	Post-HWE green tea leaves	DME extraction			
		Tea leaves residue	Organic compounds	Water	Loss
Total (%)	100.0	28.4	1.6	70.0	–
Caffeine (μg/g)	1,210	Nd	47	498	665
Catechins (μg/g)					
C	105	41	3	35	26
EC	798	201	16	342	239
GC	587	175	7	239	166
EGC	3,568	1,256	32	1,395	885
CG	79	42	4	28	5
ECG	1,574	740	42	510	282
GCG	362	187	7	110	58
EGCG	7,437	4,164	95	2,163	1,015

Nd not detected, *DME* dimethyl ether, *C* catechin, *EC* epicatechin, *GC* gallocatechin, *EGC* epigallocatechin, *CG* catechin gallate, *ECG* epicatechin gallate, *GCG* gallocatechin gallate, *EGCG* epigallocatechin gallate

5.4.4 Properties of Extracted Components and Dewatered Bio-solids

The concentration and chemical compositions of the extracts derived from different extraction solvents were different sometimes despite the slight changes in the extraction conditions. Herein, two recent results obtained using the DME method on the extraction of natural products were presented. In the first example, the extractions of caffeine and eight catechins including catechin (C), epicatechin (EC), gallocatechin (GC), epigal- locatechin (EGC), catechin gallate (CG), epicatechin gallate (ECG), gallocatechin gallate (GCG), and epigallocatechin gallate (EGCG) from green tea leaves were studied [18]. Table 5.2 shows the concentrations of caffeine and catechins in the residue, organic extracts, and removed water. The amounts (mass) of residue, organic extracts, and removed water from 100.0 % of green tea waste were found to be 28.4 %, 1.6 %, and 70.0 %, respectively. Kanda et al., evaluated the distribution of caffeine and catechins in the samples after DME extraction. Probably, the losses in the contents of caffeine and catechins, as shown in Table 5.2, were due to the differences in the analysis methods used for wet green tea leaves (and its residue), and organic compounds and water. As shown in Table 5.2, no caffeine was detected in the residue, indicating the good extractive ability of the DME method for removing caffeine from such biological materials. Of the removed caffeine, 41.2 % was present in water, which implied that the removed water might not be suitable for low-caffeine applications without additional treatment. All the catechins were detected in the residue, extracts, and water. However, we found that the catechins remained in the residue and water rather than in the organic extracts, probably because they migrated to the water layer from the upper DME-organic layer with the evaporation of DME (refer to Fig. 5.4). Approximately 29.1–42.9 %

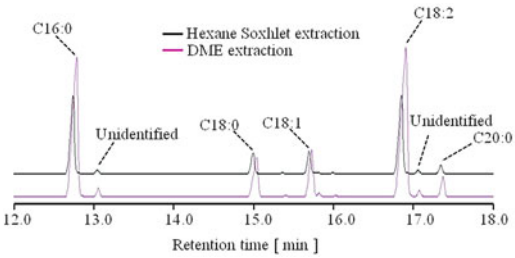

Fig. 5.10 Gas chromatogram of lipids derived from coffee grounds via DME and hexane Soxhlet extraction

Table 5.3 Proximate analysis and main elemental compositions of extracted lipids and dewatered solids from vegetal biomass

	Coffee grounds		Microalgae (*Kanogaw*)	
Analysis (wt.% dry basis)	Lipids	Solids	Lipids	Solids
Proximate analysis				
Ash yield	Nd	1.9	1.1	7.5
Volatile matter	–	81.1	–	80.1
Fixed carbon	–	17.0	–	12.4
Ultimate analysis				
C	77.0	51.5	70.9	46.9
H	11.4	6.97	10.0	6.65
N	1.96	2.43	2.62	10.7
O	9.60	37.1	15.0	27.8
S	–	0.15	0.16	0.41
HHV (MJ kg^{-1})	38.9	21.1	33.8	18.3

of the catechins were extracted into the water fraction while 25.2–56.0 % remained in the residue after DME extraction. Here, it was noteworthy that 56.0 % of the most important catechin, EGCG, still remained in the residue after DME extraction.

In the case of the extraction of lipids from spent coffee grounds, the chemical compositions of the lipids extracted using liquefied DME were determined and compared to those extracted using the Soxhlet method involving hexane. As shown in Fig. 5.10, the gas chromatograms of the lipids obtained via DME extraction resembled those obtained using the Soxhlet extraction with hexane; the carbon number of the detected lipids was in the range of C16–C18, which consisted of both saturated and unsaturated fatty acids. This outcome was almost identical to a previous report on the lipids derived from spent coffee grounds [20].

As mentioned earlier, this DME based technology can produce not only organic extracts but also dried bio-solids as byproducts. For example, the properties of the extracts and bio-solids derived from the spent coffee grounds and microalgae are shown in Table 5.3. The concentrations of carbon and hydrogen in the lipids of both spent coffee grounds and algae are higher, while nitrogen and oxygen are lower compared to those in the solids. The higher heating values (HHVs) of the lipids derived from either spent coffee grounds or microalgae are equivalent to those of

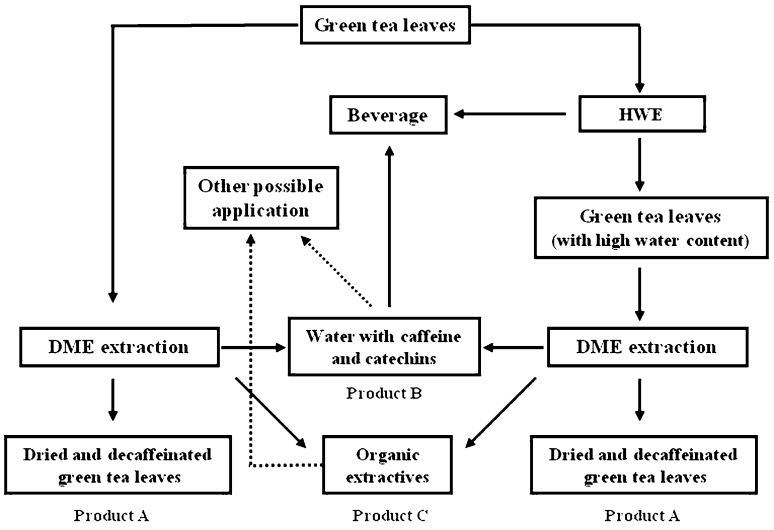

Fig. 5.11 Proposed utilisation of the DME method in the tea industry

the first-generation biodiesel, and are essentially the same as the traditional fossil oils [3]. In addition to the lipids, the bio-solids derived from both the spent coffee grounds and microalgae via DME extraction also retained sufficient calorific density to render themselves as potential carbon neutral fuels.

5.4.5 Future Possible Applications of DME Extraction

Owing to the unique properties of DME, this technique could be applied in the extraction of natural products in several industrial fields. Here, two possible applications of this technique were proposed for the tea industry and renewable bio-fuel production from vegetal biomass. The utilisation of the DME method in the tea industry has been depicted in Fig. 5.11. The right side in the figure has been conceptualised according to the outcomes of a recent study [18]. Here, the high-moisture green tea leaves after hot water extraction (HWE) are treated with liquefied DME. As mentioned earlier, it is different from the conventional method for that the DME method can simultaneously dewater (i.e. drying) and directly extracts the organic constituents from the natural feedstock at room temperature. This means that the heating of the extractant and the downstream hot-drying are both unnecessary. Furthermore, DME is a safe solvent and does not remain stable at room temperature. As a result, DME can be used for food processing. Therefore, the product B can be used for beverage production either with or without pre-treatment. The dried and decaffeinated product A can be used for the production of powdered

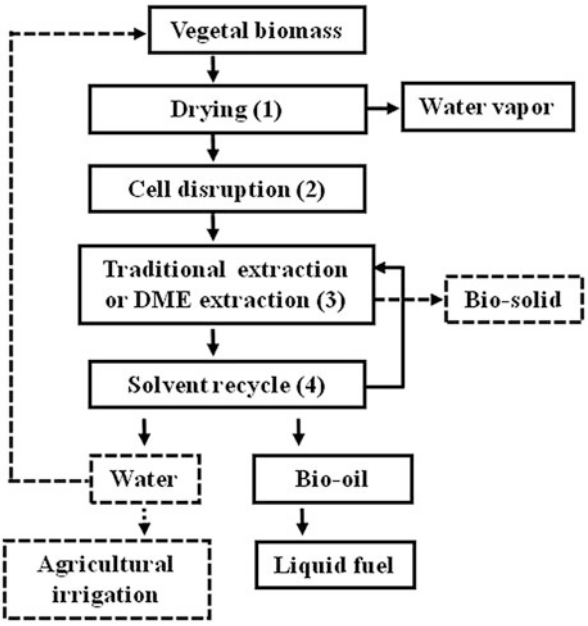

Fig. 5.12 Proposed utilisation of the DME method in the algae bio-fuel production compared to traditional method

green tea. The left side in the figure is a prospective concept derived from this study. Here, the green tea leaves could be extracted directly using the DME method without HWE. Thereupon, the amounts of caffeine and catechins in product B and catechins in product A should be much higher than those remaining post-HWE. Finally, the chemical compositions of product C from green tea leaves either with or without HWE should be further studied carefully because such condensed organic extracts from tea leaves usually contain other bio-active components, which may be of commercial value.

For the production of renewable bio-fuels, the DME technique is advantageous over the traditional extraction technologies [14, 16, 17, 22]. Herein, both traditional and DME approaches were integrated in a graphic illustration as shown in Fig. 5.12. There are four main steps: drying, cell disruption, solvent extraction, and solvent recycling, numbered as steps 1, 2, 3, and 4, respectively. In the traditional method, all four steps are normally required. The product obtained from the traditional method is only bio-oil, which can be chemically converted into liquid bio-fuels such as biodiesel. The water contained in the biomass is vaporized in step 1 in the traditional method, and the disposal of the biomass residues needs to be considered. In the DME approach, only steps 3 and 4 are required because of the dewatering ability and penetrability of DME. Besides the main product of bio-oil, the byproducts, namely dewatered bio-solids and removed water, could also be meaningfully utilised. For example, if the removed water from the vegetal feedstock did not contain any DME at room temperature, then such water could be used for agricultural irrigation.

5.5 Conclusions and Future Applications

In comparison to the traditional solvent extraction technology and SFT, the DME extraction has many advantages, particularly for natural product extraction from high moisture containing natural feedstock. As an organic solvent, liquefied DME is water-soluble; therefore, water can be removed from the feedstock simultaneously with the organic components. The boiling point of DME is close to the room temperature; therefore, the circulation of DME (gasification and liquefaction) is efficiency in energy consumption. The safety of DME allows for the application of this technique to the pharmacy and food industries. Above all, the uniqueness of this technique lies in the fact that it couples both dewatering and extraction, and therefore, both extracted chemicals and residue are obtained as products. However, as a new technique, some certain phenomenon such as the excellent penetrability of DME, needs to be clarified further. Additional efforts should also be directed toward testing other sources of natural feedstock, and expanding the possible application of this technique to other fields. A pilot-scale study should also be carried out to make this technique industrially practicable as soon as possible.

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